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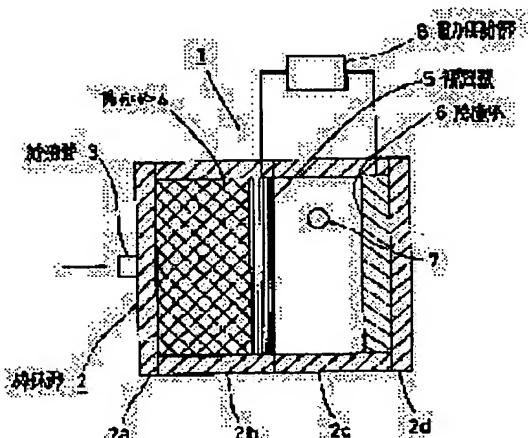
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## (54) PLATING SOLUTION PRETREATING DEVICE AND ELECTROLYTIC ELECTRODE

## (57)Abstract:

PURPOSE: To remove halide ions from halide ion contg. plating solution before plating treatment.

CONSTITUTION: An anodic body 4 consisting of a mesh structural body and a cathodic body 6 are arranged in a frame body 2 and simultaneously a solution feed pipe 3 and solution discharge pipe 7 are arranged so that plating solution may flow in the anodic body 4. A chloride ion contg. sulfate solution, for example, is forcibly fed to the frame body 2 from the solution feed pipe 3 and power is applied between the anodic body 4 and the cathodic body 6. Since the anodic body 4 has large electrode surface area and low current density, the generation of oxygen of high limiting current density is restrained to selectively gasified chloride ions, causing them to be removed as gaseous chlorine. The sulfate solution given electrolysis treatment is led to an open vessel from the solution discharge pipe 7 and given vapor-liquid separation by air bubbling to rapidly remove gaseous chlorine and after that, it is used in plating treatment as plating solution.



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CLAIMS

## [Claim(s)]

[Claim 1] The pre-treatment equipment of the plating liquid characterized by to form a liquid flow so that plating liquid may carry out conduction of the anode plate inside of the body while having the cell for pretreating the plating liquid before the plating processing containing halogen ion, and the insoluble anode plate object which consists of the cathode object and the mesh structure which have been arranged in this cell and removing the halogen ion in plating liquid through the current between the anode plate object and the cathode object.

[Claim 2] The pre-treatment equipment of the plating liquid according to claim 1 which established the bubbling means for separating the halogen gas which carried out bubbling into the plating liquid after electrolysis, and occurred by electrolysis from plating liquid.

[Claim 3] The electrode for electrolysis characterized by coming to have the polar zone which consists of the conductive mesh structure, and the electric supply section which supplies power to this polar zone.

[Claim 4] It is the electrode for electrolysis according to claim 3 which joins on the surface of the polar zone, prepares the conductive back up plate in which many holes were formed, and is characterized by this back up plate coming to make the electric supply section serve a double purpose.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to the pre-treatment equipment and the electrode for electrolysis of plating liquid for removing the chlorine ion contained during a plating bath, when forming a track in the through hole of a printed circuit board by electroplating.

#### [0002]

[Description of the Prior Art] In order to form a track in the through hole of a printed circuit board by coppering conventionally, while using as an anode plate object the ball-like Lynn content copper put into the titanium basket, said printed circuit board is used as a cathode object, these electrode object is arranged in the cell which filled the plating bath, and, generally the approach of carrying out electroplating is adopted.

[0003] However, periodically, since according to this approach copper dissolved into an electrolytic solution and an electrode was exhausted from said anode plate object, although the anode plate object needed to be exchanged, since it was expensive, the Lynn content copper of the shape of said ball had the problem that the costs which plating processing takes soared.

[0004] Plating processing can be performed also by the approach of on the other hand electrolyzing the solution of sulfates, such as a nickel sulfate, the plating bath, for example, the copper sulfate, containing a plated metal, using an insoluble anode as an anode plate object. Although it is a cheap approach compared with the case where can obtain a copper-sulfate solution and Lynn content copper is made into the source of plating by dissolving copper carbonate into a sulfuric-acid solution in this case, since the cupreous chloride is used for the process top raw material, in copper carbonate, the chlorine root is contained at the minute amount.

#### [0005]

[Problem(s) to be Solved by the Invention] However, if it mixes during a sulfate plating bath more than a certain amount of [ a chlorine ion ] concentration, the front face of the plated body will turn into a split face, or will become the shape of a phyma, and the cause of raising a poor product, such as projecting needlelike. For this reason, although the method of pressing down a poor product by adding the additive of the organic substance or an inorganic substance during a sulfate plating bath, and removing a chlorine ion is taken, since a chlorine ion is fully unremovable also by such approach, when it is limited and the tolerance limit of a product is exceeded, in order to have to discard a sulfate plating bath, the costs of abandonment processing also serve as this thing.

[0006] This invention is made by the basis of such a situation and the purpose is in offering the pre-treatment equipment of the plating liquid for removing halogen ion effectively out of the plating liquid containing halogen ion, such as a chlorine ion. Moreover, other purposes are to offer the electrode with a low electrode overvoltage for electrolysis.

#### [0007]

[Means for Solving the Problem] This invention is characterized by to form a liquid flow so that plating liquid may carry out conduction of the anode plate inside of the body while it is equipped with the insoluble anode plate object which consists of the cathode object and the mesh structure which have been arranged in the cell for pretreating the plating liquid before the plating processing containing halogen ion, and this cell and removes the halogen ion in plating liquid through a current between an anode plate object and a cathode object. In this case, it is desirable to establish a bubbling means and to separate promptly the halogen gas which occurred by electrolysis from the electrolytic solution.

[0008] Moreover, other invention is characterized by coming to have the polar zone which consists of the conductive mesh structure, and the electric supply section which supplies power to this polar zone.

#### [0009]

[Function] For example, by electrolyzing the plating liquid which contains a chlorine ion as halogen ion, the chlorine ion in plating liquid is gasified, and serves as chlorine gas, and this chlorine gas is removed out of plating liquid by carrying out bubbling of the air for example, within an open container.

[0010] Here, as an anode plate object, since [ that an electrode surface product is large ] the mesh structure, such as being curdy (the shape of a nonwoven fabric), is used and the shape of sponge, fibrous, or current density in an anode plate object can be made low, for example, generating of oxygen gas with limiting current density higher than chlorine gas can be suppressed, a chlorine ion can be gasified alternatively, and it can remove as chlorine gas.

[0011] Therefore, by using the sulfate solution from which the chlorine ion was removed by such pretreatment as a plating bath, the front face of the plated body can turn into a split face, or generating of the shape of a phyma or a poor product, such as projecting needlelike, can be suppressed.

[0012] Moreover, the electrode for electrolysis which consists of the conductive mesh structure used as an anode plate object here can also be used as a cathode object, and is applicable to various electrolysis reactions besides the reaction which removes a chlorine ion from a sulfate solution further. And since the apparent surface area of the electrode for this electrolysis is large, it can make the overvoltage of an electrode low, therefore can suppress generating of side reaction, and can advance the electrolysis reaction of the purpose efficiently.

#### [0013]

[Example] Drawing 1 and drawing 2 are the sectional views and appearance perspective views of a pre-treatment equipment 1 of

plating liquid concerning the example of this invention, respectively.

[0014] Two in drawing 1 is the frame section which constitutes a cell, four frame 2a which consists of acrylic resin, 2b, and 2c and 2d are inserted in this order free [ attachment and detachment ], and this frame section 2 is constituted.

[0015] The liquid supply tubing 3 for introducing the sulfate solution which is the plating liquid before the plating processing containing a chlorine ion in the frame section 2 is formed near the center section of said frame 2a. And into said frame 2b, dense ON of the anode plate object 4 with 100mm of \*\*\*\*, 100mm of horizontal abbreviation, and magnitude with a thickness of about 20mm is carried out. this anode plate object 4 put in and carried out expanded one of the slitting — it is — it is — for example, it carried out punching and made the hole, it consists of titanium, and location immobilization is pressed down and carried out by the conductive back up plate 5 with the almost same magnitude as the projected area of the anode plate object 4 at the frame 2a side. And this back up plate 5 is connected with the power feed zone 8.

[0016] Said anode plate object 4 is made using the carbon—for example system ingredient which is an insoluble solution, such as a metal, noble metals, carbon, or graphite, at the time of energization in the sulfate solution. Moreover, so that current density in the anode plate object 4 can be made low as structure of the anode plate object 4, generating of oxygen gas can be suppressed and the chlorine ion contained in a sulfate solution by this can be alternatively generated as chlorine gas The shape for example, of sponge which enlarged the electrode surface product, fibrous, or the mesh structure which spreads in the direction of three dimensions, such as being curdy (the shape of a nonwoven fabric), is adopted.

[0017] The cathode object 6 with the almost same magnitude as the projected area of the anode plate object 4 carries out dense ON, location immobilization is carried out and the power feed zone 8 is connected to this cathode object 6 so that it may counter with the anode plate object 4 in said frame 2c. Moreover, since electric anticorrosion of the cathode object 6 is carried out if a cell is in an energization condition, a griddle, a copper plate, or a stainless plate can be used in quality of the material. However, since there is fear of the dissolution of a cathode body constituent or remelting of a deposit metal when energization is stopped leaving the electrolytic solution in a cell, as for after an energization halt, it is desirable to provide the means of pure water washing. Furthermore, the drainage tube 7 is formed near the side-face upper part of the space near side of drawing 1 of this frame 2c, and this drainage tube 7 is connected to the open container 72 equipped with the powder trachea 71 which is a bubbling means.

[0018] Next, an operation of an above-mentioned example is described. While feeding the plating liquid containing the chlorine ion before plating processing, for example, a sulfate solution, in the frame section 2 through the pump which is not illustrated from the liquid supply tubing 3, power is supplied from the power feed zone 8, and between the anode plate object 4 and the cathode object 6 is energized. At this time, power is supplied to the anode plate object 4 through the back up plate 5.

[0019] While a sulfate solution carries out conduction of the inside of the anode plate object 4 in the direction of board thickness, is further extruded through the mesh of the back up plate 5 at the cathode object 6 side and is sent to the open container 72 through the drainage tube 7, since the chlorine ion contained in the sulfate solution is gasified in the anode plate object 4, and serves as chlorine gas and supply of the electrolytic solution in an anode plate and a permutation are also performed easily, gasification of a chlorine ion is performed smoothly. Furthermore, the sulfate solution which passed the open container 72 flows in in the frame section 2 through the liquid supply tubing 3 again, and circulates through the inside of equipment. In this case, it becomes a sulfate solution from the mesh structures, such as a graphite fiber which is an insoluble solution, at the time of energization, and since [ that an electrode surface product is large ] current density is low, the anode plate object 4 suppresses generating of oxygen gas in the anode plate object 4, and a chlorine ion is gasified alternatively and it serves as chlorine gas. Moreover, if this gasified chlorine gas is left as it is, it will become the factor which it remelts [ factor ] in a sulfate solution and worsens current efficiency, but since the sulfate solution discharged from the drainage tube is led to the open container 72, vapor liquid separation is promptly carried out by bubbling of air and chlorine gas is removed, high current efficiency is acquired.

[0020] in this way, the anode plate side which is not illustrated using as a plating bath, the sulfate solution, for example, the copper-sulfate solution, pretreated (removal processing of a chlorine ion), — an insoluble anode — moreover, the plated body, for example, a print machine hill, is arranged to a cathode side, and coppering processing is performed to a printed circuit board.

[0021] When the inside of above equipment was circulated for the sulfate solution, having used the flow rate of liquid as a part for 600ml - 1200ml/, and having used the energization current as 1.0 A/dm<sup>2</sup> for the resistance welding time for 6 hours with the equipment applied to an above-mentioned example as said sulfate solution here using a copper-sulfate solution and a nickel-sulfate solution and removal processing of a chlorine ion was performed, the result shown in Table 1 was obtained.

[0022]

[Table 1]

溶液名	硫酸銅溶液	硫酸銅溶液	硫酸ニッケル溶液	硫酸ニッケル溶液
データ項目				
銅イオン濃度 (g/L)	18	40	—	—
ニッケルイオン濃度 (g/L)	—	—	30	20
硫酸濃度 (g/L)	180	150	170	180
塩素イオン濃度 (ppm)	140	120	350	145
通電電流 (A/dm <sup>2</sup> )	1.0	0.5	1.0	1.0
6時間後の塩素イオン濃度 (ppm)	10	40	190	10
平均電流効率 (%)	12	10	14	14

If the concentration of the chlorine ion in plating liquid is decreasing or less to 1/10 in what has a high elimination factor, therefore performs plating processing with these plating liquid by performing above-mentioned pretreatment so that this result may show, flattening of the plated body is attained, a front face will become coarse or the shape of a phyma and the poor product of projecting needlelike will be improved.

[0023] Moreover, frame 2a, 2b, and 2c and 2d, since it removes and has easy structure, the metal which deposits in cathode 6 can be removed easily, respectively.

[0024] Although power is supplied above through the back up plate 5 by this invention at the anode plate object 4, you may make it supply direct power to the anode plate object 4.

[0025] In addition, the copper carbonate which can also use a copper-sulfate solution, an iron-sulfate solution besides a nickel sulfate, etc. as said sulfate solution, and contains a chlorine root as said copper-sulfate solution may be dissolved into a sulfuric-acid solution. Furthermore, as plating liquid, you may be things other than a sulfate solution again.

[0026] Next, the electrode for electrolysis is explained. In order to advance efficiently a electrolysis reaction which is performed with the pre-treatment equipment of above-mentioned plating liquid, it is easiest to make an energization current increase. However, since an overvoltage will also rise if an energization current is made to increase and the current density to an electrode surface is made to increase, side reaction may occur with the reaction of the purpose. Especially, when the reaction of the purpose is low in potential, or in being the reaction for which potential tends to rise that concentration is thin and diffusion tends to become rate-limiting, side reaction poses a problem being easy to happen. For example, in the pre-treatment equipment of above-mentioned plating liquid, since the concentration of the chlorine ion contained in plating liquid is thin, an oxygen evolution reaction with limiting current density higher than a chlorine generating reaction occurs as side reaction, and it has become the cause of worsening the effectiveness of chlorine removal.

[0027] Although it is necessary to lower an overvoltage to extent which suppresses side reaction in order to solve such a problem, the method of making the area of an electrode increase from the former in this case, seeing, and dropping the upper current density is taken. However, in the metal tabular electrode which must be increased so that the projected area of two poles may become equal, and is used conventionally, if the area of one electrode is made to increase, since it is the 2-dimensional planar structure, there is a limit in the increment in area in tooth space, and the area of a counter electrode is not an effective approach, either.

[0028] So, in the above-mentioned example, the solution in question is aimed at by making structure of the electrode for electrolysis into the mesh structure which spreads in the direction of three dimensions. That is, since the surface area of an electrode increases with such structure, the overvoltage of an electrode can be made low, the oxygen evolution reaction which is side reaction as a result is suppressed, and a chlorine generating reaction advances efficiently.

[0029] An example of the electrode for electrolysis of such structure is shown in drawing 3 R>3 and drawing 4. It is a cell for ten in drawing to perform a electrolysis reaction, and the polar zone which 41 consists of the conductive mesh structure which spreads in the direction of three dimensions, for example, makes an anode plate, and this polar zone 41 consists of for example, graphite fiber fiber. The diameter of fiber of graphite fiber fiber is dozens of micrometers – about hundreds of A, and the mesh structure is formed by weaving this fiber in the shape of a cross, or making it into the shape of a nonwoven fabric. The mesh structure is a three-dimensional structure object of a transparency mold which it has [ object ] thickness and can carry out conduction of the solution to itself here. And although the thickness of the polar zone 41 is determined in consideration of the omission effectiveness of an electrolytic current consistency, the electrolytic-solution rate of flow, and generating gas, it is effectively used, for example by about 10-20mm.

[0030] And the conductive back up plate 51 in which many holes were formed is joined and formed in the front face of this polar zone 41. This back up plate 51 is formed by putting slitting with a die length of about 10mm into the metal plate which consisted of the insoluble quality of the materials even if it had the almost same magnitude as the projected area of the polar zone 41, for example, carried out positive polarization in service-condition baths, such as titanium (Ti), and platinum (Pt), gold (Au), at intervals of about 3mm, and carrying out expanded one to it, or making a hole by punching. Moreover, this back up plate 51 is connected with the power feed zone 8, and the polar zone 41 and the back up plate 51 are being further fixed by the frame part 9.

[0031] Moreover, it has the almost same magnitude as the projected area of the polar zone 41 in the location where the electrode for

electrolysis in a cell 10 countered, for example, the counter electrode (cathode) which consists of iron (Fe), stainless steel, nickel (nickel), etc. is arranged, and this counter electrode 61 is also connected to the power feed zone 8.

[0032] And in the electrode for electrolysis constituted in this way, the back up plate 51 acts on the polar zone 41 as the electric supply section for supplying power to homogeneity, power is supplied to the polar zone 41 through the back up plate 51 from the power feed zone 8, and between the polar zone 41 and counter electrodes 61 energizes it. (It is in the inclination [ made / for contact resistance to decrease / better / current efficiency ] made to increase the touch area of the polar zone 41 and the back up plate 51 here.) And the electrolytic solutions, such as the plating liquid containing the chlorine ion before plating processing, for example, a sulfate solution etc., carry out conduction toward a counter electrode 61 from the polar zone 41, as the drawing 3 Nakaya mark shows, and a electrolysis reaction is performed.

[0033] Since the polar zone 41 is the conductive mesh structure which spreads in the direction of three dimensions and has current distribution also in the plate thickness direction at this time, it sees by the conduction of the electrolytic solution and the upper electrode surface product increases. Therefore, since an electrode overvoltage becomes low, an oxygen evolution reaction is suppressed, a chlorine generating reaction advances alternatively, and chlorine removal can be performed effectively.

[0034] The presentation experimented in chlorine removal of the copper-sulfate solution of copper-sulfate concentration 50 g/L and sulfuric-acid concentration 180 g/L, and actually checked the effectiveness of the above-mentioned electrode for electrolysis. The used electrodes for electrolysis were wide [ which consist of graphite fiber fiber / 100mm long and 100mm wide ], and a graphite fiber electrode (GFE) with a thickness of 20mm, under electric-field current density 0.5 A/dm<sup>2</sup>, receiver solution 5L, Cell Volume 400mL, and the conditions of SV=90 (it means that 90 times Cell Volume per hour places and changes.), performed the electrolysis reaction at the room temperature, and measured the level of chlorine in a solution. Moreover, the same experiment was conducted as comparative experiments, using a graphite plate electrode (GBE) as an electrode for electrolysis. A graphite plate electrode forms a hole with a diameter of 5mm in 100mm long, 100mm wide, and a graphite plate with a thickness of 10mm at intervals of 10mm. These experimental results are shown in drawing 5 as a graph which shows the relation of the residual chlorine concentration in time amount and a solution. Moreover, in drawing 5, the curve drawn as the continuous line shows the result at the time of using a graphite fiber electrode, and the curve drawn by the dotted line shows the result at the time of using a graphite plate electrode.

[0035] From this result, when a graphite fiber electrode was used as an electrode for electrolysis, it has checked that the residual chlorine concentration in a solution was far low, therefore the removal effectiveness of chlorine was higher than the case where a graphite plate electrode is used.

[0036] Since the electrode for electrolysis of this example is the mesh structure which spreads in the direction of three dimensions as stated above, an apparent area of an electrode increases and it becomes possible to make an electrode overvoltage low. For this reason, also in reactions in which side reaction tends to occur, such as a reaction for which potential tends to rise that a reaction and concentration low in potential are thin, and diffusion tends to become rate-limiting, side reaction is suppressed and it becomes possible to advance the reaction of the purpose effectively.

[0037] In addition, you may make it the electrode for electrolysis of this example supply power to the direct polar zone 41 from the power feed zone 8 without the back up plate 51. Moreover, the electrode for electrolysis of this example is possible also for using it as cathode, and usable as various electrodes for a electrolysis reaction other than the reaction which removes a chlorine ion from a sulfate solution further.

[0038]

[Effect of the Invention] According to this invention, it is insolubility, and as an anode plate object, to the electrolytic solution containing halogen ion, since [ that an electrode surface product is large ] the mesh structures, such as a graphite fiber, were used, for example, as it already explained in full detail, halogen ion can be gasified alternatively, and it can remove efficiently as halogen gas. Furthermore, by establishing a bubbling means, halogen gas can be removed much more efficiently. Therefore, since a poor product, like the front face of the plated body turns into a split face by using the plating liquid which performed such pretreatment is improvable, while being able to aim at improvement in the product yield, since [ that the price currently used conventionally is high ] it is not necessary to use ball-like Lynn content copper, for example, the costs which plating processing takes can also be reduced.

[0039] And while according to the polar zone using the mesh structure electric power can be supplied to the whole polar zone and electrode reaction advances efficiently by joining the conductive back up plate in which the overvoltage could be made low, and side reaction could be suppressed, and many holes were formed on the surface of the polar zone, without enlarging the polar zone, reinforcement sufficient as an electrode is securable.

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## DESCRIPTION OF DRAWINGS

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**[Brief Description of the Drawings]**

[Drawing 1] It is the sectional view of the pre-treatment equipment of the plating liquid concerning this invention.

[Drawing 2] It is the appearance perspective view of the pre-treatment equipment of the plating liquid concerning this invention.

[Drawing 3] It is the sectional view of the electrode for electrolysis concerning this invention.

[Drawing 4] It is the perspective view of the electrode for electrolysis concerning this invention.

[Drawing 5] It is the graph which shows the relation of the residual chlorine concentration in time amount and a solution.

**[Description of Notations]**

1 Pre-treatment Equipment of Plating Liquid

2 Frame Section

3 Liquid Supply Tubing

4 Anode Plate Object

41 Anode Plate Section

5 51 Back up plate

6 61 Cathode object

7 Drainage Tube

71 Powder Trachea

72 Open Container

8 Power Feed Zone

9 Frame Part

10 Cell

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[Translation done.]